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PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES INDIA

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PARTS IV-V]

SECTION A

[VOL. 23

BI-PLANER PERIODIC ARRANGEMENT OF ELEMENTS

Part I. Classification on Chemical Grounds

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Read on May 8, 1954

(Communicated by Dr. S. P. Mitra)

To the present day many attempts have been made to draw a perfect Periodic Table of elements⁷ but none successfully accomplished. The space models of Crookes, Emerson, Soddy, Harkins and Hall, Schaltenbrand, Payne,⁶ Wrigley,⁹ Clauson¹ and Horie² are too cumbersome for convenient use. In comparison to these, various modifications of Mendeleeff's chart,⁷ viz., long chart (Werner type), long chart (Bayley type), Spiral (Baumhaver type), Helical (Harkins type), long chart (Luder type),⁴ Spiral (Irwin type),³ short chart (McCutcheon type),⁵ short chart (Sanderson type)⁸, etc., are much simpler but they too show break of periodicity at various places and suffer from one or other of the following defects as pointed out by Zmaczynski¹⁰ and Luder.⁴

DEFECTS OF THE ONE-PLANER TABLES

(1) The different classes of elements, viz., (a) the metals, non-metals, metalloids; (b) normal elements, transitional elements, rare earth elements; and (c) amongst metals highly basic and less basic metals are not distinctly separated from one another. By placing all types of elements together as

those of the Mn group with Cl group or the Alkali group with the least basic metallic group of copper, a great confusion has been manifested in these tables.

(2) Elements that yield colourless and diamagnetic ions are indistinguishable from those which give coloured and paramagnetic ions.

(3) Such tables have no place for rare earth metals. Their positions in one square or as a separate series of fourteen elements outside the table make these tables rather unscientific and defective. None of these tables is capable of revealing similarities and dissimilarities in the properties of rare earth elements.

(4) The tables do not picture the electronic configuration of the atoms.

(5) The tables are incapable of generalising the data in various fields of chemistry, *e.g.*, catalysis, adsorption, heat of solutions, melting point of compounds, complex formations, etc.

(6) The failure of the tables to retain beyond the third period the continuous variation of properties from active metal to active non-metal with the addition of electrons to the outermost shell of the atoms.

Mendelleeff's short chart suffers from all the abovementioned defects. Long charts overcome the first three of the defects to some extent, but still suffer from the last three and greatly exaggerates the sixth. Long charts introduce non-existent breaks between Be and Bo, and Mg and Al. Above all, the greatest defect of long charts is that due to the larger number of groups in them (18 or 32) they lack in "Compact Simplicity" which is the ultimate requirement of a periodic table.

The problem now is to seek an arrangement in which there are mainly eight groups and at the same time different family of elements may have their separate apartments. The author has succeeded in framing a bi-planer arrangement of elements in which not only these two requirements have been realised but also all the abovementioned anomalies have been removed. The atomic number rule is followed rigidly. Herein only special features of the arrangements have been mentioned just to acquaint one with this new form of table and its profound utility in science.

DESCRIPTION OF THE TABLES

In this arrangement the normal elements of each period which follow the periodic law in all respects, have been placed in the front plane. The remaining elements are metals and as such they cannot be placed along with the non-metals of 4th, 5th, 6th, 7th and 8th groups nor can they be grouped

along with highly basic alkali and alkaline earth metals. The transitional and rare earth metals have, therefore, been classified along with 3rd group metals, but due to their dissimilarity to normal elements, they are kept separated from the latter by disposing them over an Extension or Projection Plane of the third group, situated perpendicular to the front plane. The third group extension plane is again divided into eight groups and seven periods; 0 and 7th groups have been further divided into A and B sub-groups, and thus ten elements of each transitional series have been placed only in eight groups in the manner shown in the table. Out of the twenty-four non-normal elements of sixth and seventh periods, ten transitional elements of each are arranged in a manner already described; the remaining fourteen rare earth elements are arranged in seven groups from 1 to 7 each containing a pair of elements. Thus fourteen rare earth elements from Cerium (58) to Lutecium (71) of sixth period are placed between the elements Lanthanum (57) and Hafnium (72) in seven groups. The Actinide series of elements of seventh period are arranged in a manner analogous to sixth period rare earth series. The rare earth elements do not occupy the positions between the transitional elements.

SPECIAL FEATURES OF THE TABLE

The different classes of elements, *viz.*, (a) metals, non-metals, metalloids; (b) normal elements, transitional and rare earth elements; and (c) amongst metals highly basic and less basic metals are distinctly separated from one another, and thus great simplicity has been obtained in the table.

By keeping eight groups in the Front-plane, the Compact Simplicity of the Mendeleeff's short chart is maintained as such.

The non-existing break between Beryllium and Boron groups that occurs in long charts, has been eliminated and at the same time the atomic number rule is rigidly followed.

The table retains beyond the third period the continuous variation of properties from active metal to active non-metal as electrons increase in the outermost shell of the atoms.

The elements that yield colourless and diamagnetic ions are distinguished from those that yield coloured and paramagnetic ions. The elements of the front plane and those belonging to the extreme groups in the extension plane, give colourless diamagnetic ions. Thus in transitional series, ions of scandium and zinc family elements on one side and monovalent ions of copper family on the other are colourless and diamagnetic in nature. In

Bi-planer Periodic Arrangement of Elements
Front Plane

↓ Periods ↓	Groups →	1	2	3	4	5	6	7	8
K)	I	H 1							He 2
KL)	II	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	Ne 10
KLM)	III	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	A 18
KL MN)	IV	K 19	Ca 20	Ga (21-30) 31	Ge 32	As 33	Se 34	Br 35	Kr 36
KL MN O)	V	Rb 37	Sr 38	In (39-48) 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
KL MN OP)	VI	Cs 55	Ba 56	Tl (57-80) 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
KL MN OP Q)	VII	Fr 87	Ra 88	(89-112) 113	114	115	116	117	118

(This plane is to be placed at the back and perpendicular to the Front Plane)

Third Group Extension Plane

Periods ↓	Groups →	0		1	2	3	4	5	6	7	
		A	B							A	B
I											
II											
III											
IV		Sc 21	Zn 30	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29
V		Y 39	Cd 48	Zr 40	Nb 41	Mo 42	Ma 43	Ru 44	Rh 45	Pd 46	Ag 47
VI		La 57	Hg 80	Ce 58 Tb 65 Hf 72	Pr 59 Dy 66 Ta 73	Nd 60 Ho 67 W 74	Pm 61 Er 68 Re 75	Sm 62 Tm 69 Os 76	Eu 63 Yb 70 Ir 77	Pt 78 Au 79	Gd 64 Lu 71
VII		Ac 89	...	Th 90 Bk 97 ... 104	Pa 91 Cf 98 ... 105	U 92 ... 99 ... 106	Np 93 ... 100 ... 107	Pu 94 ... 101 ... 108	Am 95 ... 102 ... 109	... 103 ... 110 ... 111	Gm 96

rare earth series Ce, Tb, Th, Bk, and Gd, Lu, Cm. and the element of atomic number 103 give colourless ions.

Analogous to the breaks in Moseley's curve, loops in Irwin Spiral, discontinuous maxima in atomic volume curve, the extension plane in bi-planer arrangement indicates the existence, between calcium and gallium groups, of a series of elements whose properties and electronic configuration are in no way similar to those of the normal elements.

The problem of the arrangement of rare earth elements which has been an enigma to the scientists since the time of Mendeleeff has here been solved. The similarities and dissimilarities in the properties of these elements are beautifully revealed from their positions in this table. Thus the pair of elements which show similarities in various aspects are grouped together, e.g., cerium and terbium are the most easily oxidised members, praseodymium and dysprosium are oxidizable but less prominently so, europium and ytterbium are the only members of the groups which may readily be reduced to the bivalent condition. The elements which yield colourless trivalent ions are in pairs as described earlier. The table does not introduce the separation of such intimately associated pairs as zirconium and hafnium, columbium and tantalum, molybdenum and tungsten from rare earth elements whose properties are in no way similar (*vide* Hopkins, B. S., *Chapters in the Chemistry of the Less Familiar Elements*, Stipes Publishing Company, Champaign, Illinois, 1939, Vol. I, Chap. 3, p. 3). The table indicates that the elements scandium, yttrium, lanthanum and actinium are not members of the rare earth series. It also points out that elements from thorium to the element of atomic number 103 will be members of the actinide series of rare earth, from elements of atomic number 103 to 113 will belong to transitional series and then from 113 to 118 to typical elements. Beyond 118 the stability of the elements will be so much reduced that their existence will not be possible.

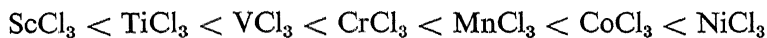
The valencies of the normal elements are indicated by their respective group numbers. Since the transitional and rare earth elements fall in the extension plane of the 3rd group, they will frequently exhibit the oxidation state of three. Variable valencies of these metals can be indicated from their positions in the table by the simple rules. Maximum valencies of elements from Zero to fifth groups can be obtained by adding their respective group numbers of the extension plane to "three", their front plane group number. Thus scandium group elements can show 3, titanium 4, vanadium 5, chromium 6, manganese 7, and iron 8 as the maximum valencies. After iron group, the minimum valencies for the seventh and eighth group

elements can be obtained by subtracting 1 and 2 respectively from the number "three". Consequently the cobalt group of elements can show a minimum valency of two, while nickel and copper group elements one.

The basicity of the extension plane elements decrease regularly with the increase of group numbers. Consequently the right-hand side members of the plane are chemically less reactive and can exist free in nature. Gold, which is situated last in the electro-motive series of elements, is also occupying the end-position in the plane.

The tendency of elements to form co-ordination compounds will be more prominent in the right-hand side members while the tendency to form polyacids, greater in left-hand side members of the extension plane.

Hygroscopic nature of the same valent metal salts of a period increases with the increase of group numbers of the metals. Thus hygroscopicity of the chlorides of IV period metals, will vary in the following order:



The same is true for the other period metals.

APPARENT DEFECTS OF THE TABLE

(1) *Grouping of Ni-Cu and Sc-Zn Elements.*—Undoubtedly these groups resemble the A and B sub-groupings of Mendeleeff's chart but they do not show such a marked divergence in the properties of elements as the VII A and VII B or I A and I B group elements in Mendeleeff's table. Here the elements of sub-groups are all metals and are very similar in many respects.

(2) *Discontinuity of Atomic Number.*—Due to a lack of visibility of the family of elements falling behind the Front-plane, there appears a discontinuity between the typical elements of second and third groups. But actually no discontinuity in atomic number exists anywhere in the table, and the elements are arranged perfectly in order of their atomic numbers.

(3) *Lack of Visibility.*—The lack of visibility of the extension plane elements when the normal elements are viewed, or of Front-plane elements when the transitional and rare earth elements are viewed, may be noted as a defect of the table; but actually this apparent limitation of the table is a boon in the study of the various classes of elements, since it obviates the confusion that is created in the minds when all the different classes of elements are viewed at a glance.

In this publication, the author has endeavoured to show the importance of the bi-planer arrangement from the chemical view-points. In the next

publication the validity of the arrangement will be discussed in the light of the electronic configuration of atoms.

My thanks are due to Prof. S. Ghosh and Dr. Bal Krishna for their keen interest in this work.

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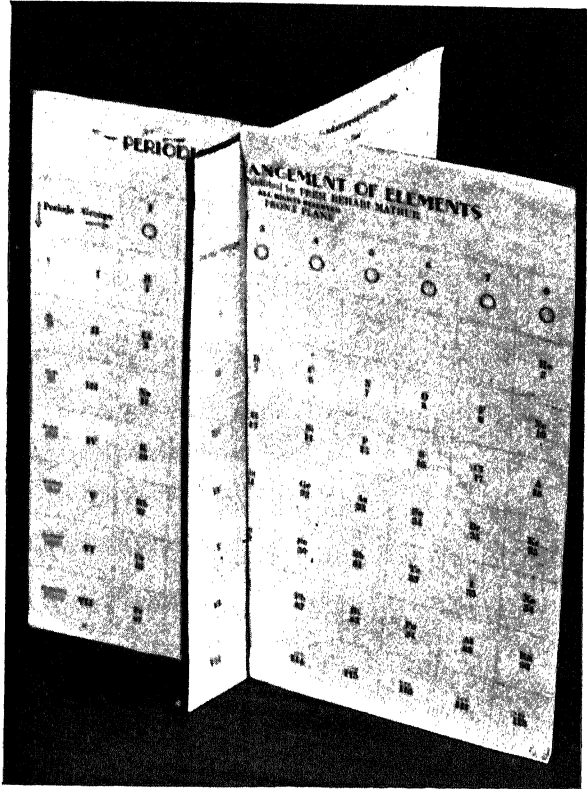


FIG. 1

A THEOREM ON SELF-RECIPROCAL FUNCTIONS

BY RAM KUMAR

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(Communicated by Prof. P. L. Srivastava)

1. The object of this paper is to give a theorem which enables us to derive new self-reciprocal functions from known ones.

A function will be said to be R_ν , if it is self-reciprocal in the Hankel-Transform of order ν .

Following Hardy and Titchmarsh, I shall say that $f(x)$ belongs to $A(a, a)$, where $0 < a \leq \pi$, $a < \frac{1}{2}$ if (1) it is an analytic function of $x = re^{i\theta}$ regular in the angle defined by $r > 0$, $|\theta| < a$ and (2) it is $O(|x|^{-a-\epsilon})$ for small x , and $O(|x|^{a-1+\epsilon})$ for large x , for every positive ϵ and uniformly in any angle $|\theta| \leq a - \eta < a$.

I will make use of the following theorem of Hardy and Titchmarsh (1930):—

A necessary and sufficient condition that a function $f(x)$ of $A(a, a)$ should be R_ν is that it should be of the form

$$f(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^{\frac{1}{2}s} \Gamma\left(\frac{1}{4} + \frac{1}{2}\nu + \frac{1}{2}s\right) \cdot x^{-s} \cdot \psi(s) ds, \quad (1.1)$$

where $\psi(s)$ is regular and satisfies

$$\psi(s) = \psi(1-s) \quad (1.2)$$

in the strip

$$a < \sigma < 1-a \quad (s \equiv \sigma + it) \quad (1.3)$$

and

$$\psi(s) = O\{e^{(\pi/4 - a + \eta)|t|}\} \quad (1.4)$$

for every positive η and uniformly in any strip interior to (1.3) and c is any value of σ in (1.3).

2. THEOREM. Let

$$Ef(x) \equiv \int_0^\infty g(xt)f(x) dx,$$

where $g(xt)$ is any arbitrary function. Then, under suitable conditions,

$$E^2 f(x) \equiv \int_0^\infty g(pt) dt \int_0^\infty g(xt) f(x) dx$$

is R_ν , if $f(x)$ is R_ν of class $A(a, a)$.

Proof.—If $f(x)$ is R_ν -function of $A(a, a)$, then, by the theorem of (1.0)

$$f(x) = \int_{c-i\infty}^{c+i\infty} x^{-s} P(s) ds,$$

where

$$P(s) = \frac{1}{2\pi i} \cdot 2^{1s} \cdot \Gamma\left(\frac{1}{4} + \frac{1}{2}\nu + \frac{1}{2}s\right) \psi(s)$$

and $\psi(s)$ satisfies all the conditions of (1.0).

Now

$$Ef(x) = \int_0^\infty g(xt) \int_{c-i\infty}^{c+i\infty} x^{-s} \cdot P(s) ds dx, \quad (2.1)$$

$$= \int_{c-i\infty}^{c+i\infty} P(s) ds \int_0^\infty g(xt) \cdot x^{-s} dx, \quad (2.2)$$

$$= \int_{c-i\infty}^{c+i\infty} P(s) \cdot G(s) \cdot t^{s-1} ds, \quad (2.3)$$

where

$$G(s) = \int_0^\infty g(x) \cdot x^{-s} dx,$$

provided we can justify the change in the order of integration.

Again,

$$E^2 f(x) = \int_0^\infty g(pt) \int_{c-i\infty}^{c+i\infty} P(s) \cdot G(s) \cdot t^{s-1} ds dt, \quad (2.4)$$

$$= \int_{c-i\infty}^{c+i\infty} P(s) \cdot G(s) ds \int_0^\infty g(pt) \cdot t^{s-1} dt, \quad (2.5)$$

$$= \int_{c-i\infty}^{c+i\infty} P(s) \cdot G(s) \cdot G(1-s) \cdot p^{-s} ds, \quad (2.6)$$

provided we can justify the change of order of integration.

Therefore

$$E^2 f(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^{\frac{1}{2}s} \cdot \Gamma\left(\frac{1}{4} + \frac{1}{2}\nu + s\right) \cdot \psi_1\left(\frac{1}{2}s\right) \cdot p^{-s} ds,$$

where

$$\psi_1(s) \equiv G(s) G(1-s) \psi(s) = \psi_1(1-s).$$

Hence the theorem follows.

3. A set of sufficient conditions for the validity of the theorem are:

(i) $g(x) = 0$ (x^{-a}) when x is small;

(ii) $g(x) = 0$ (e^{-x^b}) when x is large and $b > \frac{1}{2}$;

and (iii) $R(\nu) > -\frac{1}{2}$.

For, then, we observe that the modulus of the repeated integral (2.2) is not greater than

$$\int_{-\infty}^{\infty} 2^{\frac{1}{2}c} |\Gamma(\frac{1}{4} + \frac{1}{2}\nu + \frac{1}{2}c + \frac{1}{2}iy)| |\psi(c+iy)| dy \int_0^{\infty} x^{-c} |g(xt)| dx.$$

The inversion of the order of integration will be justified, if the two integrals separately exist.

Now, the x -integral exists if $b > 0$ and $c < 1 - a$. Also, by virtue of (1.4) and the asymptotic behaviour

$$\Gamma(\alpha + i\beta + i\gamma t) = O(e^{-\pi\gamma|t|^{1/2}} \cdot t^{\alpha-1/2}) \text{ as } t \rightarrow \infty$$

the integrand in the y -integral is

$$O\{e^{(\eta-a)|y|}\} \text{ for all } \eta > 0.$$

Hence the y -integral exists for $a - \eta > 0$.

Similarly, the change in the order of integration in (2.5) will be justified if $b > 0$; $c > a$ and $a > \pi/2b$, necessitating $b > \frac{1}{2}$.

Hence the conditions stated at the beginning of this article.

Some of the conditions stated above may be relaxed in particular cases.

4. We shall now find an R_ν -function by the help of this theorem.

Let us take the R_ν -function

$$f(x) = x^{\nu+\frac{1}{2}} \cdot e^{-\frac{1}{2}x^2}; \quad R(\nu) > -1$$

given by Bailey (1930).

Then its Meijer-Transform

$$\begin{aligned}
 F(p) &= \int_0^{\infty} e^{-\frac{1}{2}px} \cdot W_{k+\frac{1}{2}, m}(px) \cdot (px)^{-k-\frac{1}{2}} \cdot x^{\nu+\frac{1}{2}} \cdot e^{-\frac{1}{2}x^2} dx \\
 &= \frac{\Gamma(-2m) \Gamma(2m+1)}{\Gamma(-k+m) \Gamma(-k-m)} \cdot e^{\frac{1}{2}p^2} \cdot p^{m-k} \\
 &\quad \times \sum_{r=0}^{\infty} \frac{\Gamma(m-k+r) \Gamma(\nu-k+m+3/2+r)}{\Gamma(2m+1+r)} \cdot \frac{p^r}{L^r} \\
 &\quad \times D_{-(\nu-k+m+r+3/2)}(p)
 \end{aligned}$$

+ (a series obtained by replacing m by $-m$ in the above), provided $2m$ is not an integer and $R(\nu-k+3/2 \pm m) > 0$, by a result due to Jaiswal (1952).

Therefore

$$\begin{aligned}
 &\int_0^{\infty} e^{-\frac{1}{2}pt} \cdot W_{k+\frac{1}{2}, m}(pt) \cdot (pt)^{-k-\frac{1}{2}} \cdot F(p) dp \\
 &= \frac{\Gamma(-2m) \Gamma(2m+1)}{\Gamma(-k+m) \Gamma(-k-m)} \cdot t^{-k-\frac{1}{2}} \\
 &\quad \times \sum_{r=0}^{\infty} \frac{\Gamma(m-k+r) \Gamma(\nu-k+m+3/2+r)}{\Gamma(2m+1+r)} \cdot \frac{L^r}{\angle^r} \\
 &\quad \times \int_0^{\infty} p^{m+r-2k-\frac{1}{2}} \cdot e^{\frac{1}{2}p^2-\frac{1}{2}pt} \cdot D_{-(\nu-k+m+r+3/2)}(p) \cdot W_{k+\frac{1}{2}, m}(pt) dp
 \end{aligned}$$

+ a series obtained by replacing m by $-m$ in the above is R_{ν} , provided $2m$ is not an integer and $R(\nu-k+3/2 \pm m) > 0$.

The term by term integration is justified because the series represented by $F(p)$ is a uniformly convergent series of continuous functions.

Therefore, on using a result of Meijer (1941), we find that

$$\begin{aligned}
 &\sum_{r=0}^{\infty} \frac{2^r \cdot t^{-k-2} \cdot \Gamma(m-k+r)}{\Gamma(2m+1+r) \cdot \angle^r} \\
 &\quad \times \left(\begin{matrix} 2, 5 \\ 5, 4 \end{matrix} \left(\frac{2}{l^2} \left| \begin{matrix} -\frac{1}{2}-\frac{1}{2}m, -\frac{1}{2}+\frac{1}{2}m, -\frac{1}{2}m, \frac{1}{2}m, -\frac{1}{2}k-\frac{1}{2}\nu-\frac{1}{4} \\ \frac{1}{2}m+\frac{1}{2}r-k, \frac{1}{2}m+\frac{1}{2}r-k-\frac{1}{2}, \frac{1}{2}k, -\frac{1}{2}+\frac{1}{2}k \end{matrix} \right. \right) \right)
 \end{aligned}$$

+ (a series obtained by replacing m by $-m$ in the above) is R_{ν} , provided $2m$ is not an integer, $R(\nu-k+3/2 \pm m) > 0$, $R(m-k) > 0$, $R(k) < 0$, $|\arg t^2/2| < \pi$ and $t \neq 0$.

5. We shall now obtain an integral formula which enables us to derive new self-reciprocal functions from known ones.

Let us take

$$g(xt) = (xt)^{m-\frac{1}{2}} \cdot e^{-\frac{1}{2}xt} \cdot W_{k,m}(xt),$$

so that

$$Ef(x) = \int_0^\infty (xt)^{m-\frac{1}{2}} \cdot e^{-\frac{1}{2}xt} \cdot W_{k,m}(xt) \cdot f(x) dx$$

is the Varma-Transform (1951) of $f(x)$ and

$$\begin{aligned} E^2 f(x) &= \int_0^\infty (pt)^{m-\frac{1}{2}} \cdot e^{-\frac{1}{2}pt} \cdot W_{k,m}(pt) \cdot dt \\ &\quad \times \int_0^\infty (xt)^{m-\frac{1}{2}} \cdot e^{-\frac{1}{2}xt} \cdot W_{k,m}(xt) \cdot f(x) dx \\ &= \frac{\Gamma(-2m) \Gamma(2m+1) \Gamma(4m+1)}{\Gamma(\frac{1}{2}-k-m) \Gamma(3m-k+3|2)} \cdot p^{2m} \cdot \\ &\quad \times \int_0^\infty x^{-2m-1} {}_2F_1\left(\begin{matrix} m+k+\frac{1}{2}, 4m+1 \\ 3m-k+3|2 \end{matrix}; -\frac{p}{x}\right) f(x) dx \\ &\quad + \frac{\Gamma(2m) \Gamma(2m+1)}{\Gamma(\frac{1}{2}-k+m) \Gamma(m-k+3|2)} \\ &\quad \times \int_0^\infty x^{-1} {}_3F_2\left(\begin{matrix} \frac{1}{2}-m+k, 1, 2m+1 \\ 1-2m, m-k+3|2 \end{matrix}; -\frac{p}{x}\right) f(x) dx, \end{aligned}$$

provided that (i) $R(p) > 0$, $R(-a+m \pm m+1) > 0$, $R(m) > -\frac{1}{4}$ and $2m \neq \text{integer}$;

and (ii) $f(t) = 0(t^{-a})$ for $t \rightarrow 0$;

$$= 0(e^{-t^b}) \text{ for } t \rightarrow \infty \text{ and } b > \frac{1}{2},$$

is R_ν , $R(\nu) > -\frac{1}{2}$, if $f(x)$ is R_ν of $A(a, a)$.

The above double integral has been reduced to a single one on using a result due to Saksena (1953).

A particular case.—If we put $k = \frac{1}{2} - m$, we arrive at the following known results (Titchmarsh, 1937):—

The function represented by

$$\int_0^{\infty} \frac{f(x)}{x+p} dx$$

is R_ν , $R(\nu) > -\frac{1}{2}$, if $f(x)$ is R_ν of $A(a, a)$.

My best thanks are due to Dr. R. S. Varma, D.Sc., for his guidance and valuable suggestions in the preparation of this paper.

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SMALL FOURIER TERMS IN CRYSTAL STRUCTURE ANALYSIS AND RENNIGER EFFECT

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Read on December 28, 1954

WHILE carrying out crystal structure analysis by the Fourier synthesis method the correct determinations of the structure factors of weak planes are of importance on account of their large number so much so that any systematic source of error may cause appreciable errors in the synthesised structure.

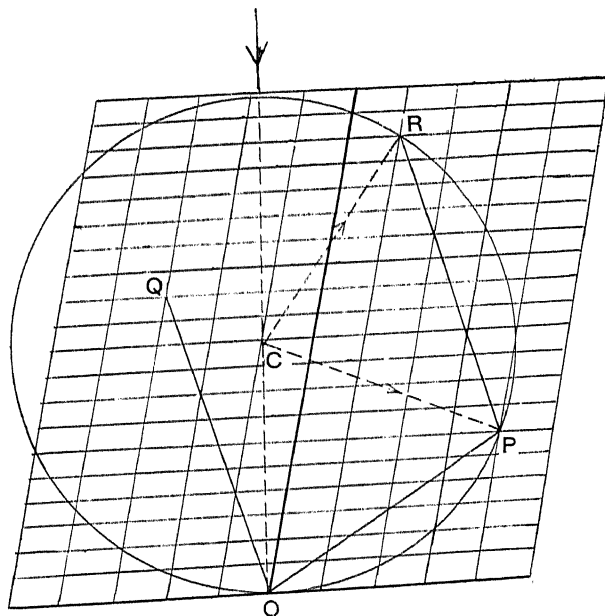


FIG. 1.

In Fig. 1, the reciprocal lattice for a crystal is represented. Suppose that the sphere of reflection which has its centre at C and passes through the origin O , also passes through two reciprocal lattice points P and R simultaneously. The vector OQ which is identical in direction and magnitude with PR will then be a reciprocal lattice vector on account of the lattice postulate.

The reciprocal lattice vector OR which is the sum of two other reciprocal lattice vectors OP and PR has its end point on the sphere of reflection simultaneously with one of the component vectors OP and if the crystal

planes corresponding to the latter two vectors are not absent planes of the crystal then on account of Renniger effect a reflection will be observed in the direction CR corresponding to reflection from a plane represented by the reciprocal vector OR even though it may be an absent plane according to the space-group of the crystal.

In cases where the resultant reciprocal vector does not correspond to an absent plane, Renniger reflection should naturally overlap with the ordinary reflection and consequently in the measurement of the integrated intensities of such planes correction due to this effect is necessary.

In an ideal case, however, such coincidences should be rather few. But on account of mosaicity of structure each reciprocal lattice point may be regarded as having a finite extension round it. Thus even when the sphere of reflection passes through this extended area P and R simultaneously, condition for the production of the Renniger effect is produced. The greater the imperfection of the crystal the greater will be the extension of the reciprocal lattice points and consequently the greater will be the probability of occurrence of Renniger effect.

On account of this finite divergence of the Bragg angle particularly in imperfect crystals, it is found that reciprocal vector of many planes of not very low indices can be represented as the vector sum occasionally of a few vector pairs that may give rise to the Renniger effect. The contributions of these vector pairs are thus added up to the real integrated intensity and so vitiates the calculation of the structure factors. The integrated intensity of the Renniger reflections for each of these pairs can be obtained by integrating the products of intensities corresponding to the extended portions of the two reciprocal points P and Q . In many cases of weak planes corrections come up to as much as the actual reflections from these planes.

But, however, if an X-ray beam of a different wave-length is incident, the size of the sphere of reflection is altered. Consequently, the condition for production of Renniger effect, *viz.*, that the passing of the sphere of reflection simultaneously through P and R will no longer hold true for these two reciprocal lattice points. So the structure factors obtained for the plane corresponding to R obtained from both the $K\alpha$ and $K\beta$ radiation will show a difference or not indicating whether anyone of them is vitiated by the Renniger effect. This gives us a way out of the difficulty.

There might however be cases where both the $K\alpha$ and the $K\beta$ reflection might be affected by Renniger effect corresponding to different pairs of planes. In that case we may compare the reflections of any plane obtained

from photographs obtained by rotations about different axes. It will be easily apparent from the figure as when one tries to rotate the sphere of reflection about OR , that it no longer passes through OP . So this is also another criterion for avoiding the Renniger error.

The methods would thus evolve naturally for the elimination of the errors due to Renniger effect are as follows. The structure factors of each of the weak reflections are determined from photographs with different rotation axes and for different wave-lengths, at least for the $K\alpha$ and the $K\beta$ radiations. The mean of the lowest group of values are adopted and at the same time care being taken that no intense Renniger pair produces that reflection.

STUDIES IN COAGULATION

Part II. Coagulation of Hydrous Ferric Oxide Sol of Different Purity and Age

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ABSTRACT

Two samples of hydrous ferric oxide sol were prepared by peptizing freshly precipitated and well washed hydrous oxide and were dialysed to give sols of different purity. Potassium sulphate solutions were added to the sols and the changes in the hydrogen ion concentration and electrical conductivity were measured.

It was observed that in all cases the sols show an increase in the alkalinity by the addition of increasing amounts of potassium sulphate. On ageing the sols liberate acid. Two or three months aged sol showed greater increase in alkalinity by the addition of potassium sulphate than that for a fresh one. On extreme ageing, however, the increase in alkalinity has a tendency to decrease.

There is also a regular decrease in the electrical conductivity of the micelle by the addition of potassium sulphate. The conductivity of the sol increases with ageing and tends to the same value on the continuous addition of potassium sulphate.

Precipitate of hydrous ferric oxide, acidified with different amounts of hydrochloric acid showed a considerable increase in alkalinity, when potassium sulphate was added to it. But on ageing, the same precipitate under similar conditions did not develop much alkalinity.

The above results have been discussed with reference to the mechanism of coagulation of the hydrous ferric oxide sol.

In previous communications¹⁻² we have reported our results on the changes of pH values during the coagulation of several hydrous ferric oxide sols by potassium sulphate. We have observed that during coagulation the systems tend to become more alkaline as shown by an increase in pH values with increasing additions of higher concentrations of potassium sulphate solutions. It has now been thought necessary to investigate the effect of age of the sol on the changes of the hydrogen-ion concentration brought about

by the coagulation with potassium sulphate. The changes in the electrical conductivity of the sol by the addition of varying amounts of potassium sulphate, both below and above its coagulation concentration have been investigated.

The adsorption of hydrogen-ions by a precipitate of hydrous ferric oxide of different ages is also measured from the pH values in the presence of potassium sulphate.

EXPERIMENTAL

Two colloidal solutions of hydrous ferric oxide were prepared by peptizing freshly precipitated and well washed, hydrated ferric oxide by A. R. hydrochloric acid and were dialyzed to different extents. The sols *A* and *B*, which were dialyzed to lesser extent were less pure than the same corresponding sols *A*₁ and *B*₁ dialysed for longer periods. The sols were analysed by the usual methods to give the following results:—

Sol	Amount per litre of the sol		Purity $\text{Fe}_2\text{O}_3/\text{Cl}^-$
	Fe_2O_3 in gm. mole	Cl^- in gm. ions	
<i>A</i>	0.1315	0.00321	40.9
<i>A</i> ₁	0.1209	0.00229	48.9
<i>B</i>	0.2457	0.07048	3.568
<i>B</i> ₁	0.2457	0.02280	10.780

The sols were then aged for different intervals of time in Jena glass bottles and to a measured volume was added known quantities of potassium sulphate solution. Keeping the total volume constant, the pH of the system was measured at a room temperature 25° C., using a glass electrode. The electrical conductivity was measured at 32° C. The specific conductivities of corresponding amounts of potassium sulphate present in the mixture of the sol were subtracted from the specific conductivities of the mixture of the sol and the electrolyte. These data represent, therefore, the changes in the electrical conductivity of the sol effected by the addition of an electrolyte. The results for such measurements are given in the following tables.

TABLE I

pH Measurements using Sol A (Purity 40.9) 10 ml. of sol taken each time (total volume 20 ml.)

K ₂ SO ₄ in ml.	pH by N/125 K ₂ SO ₄		
	Fresh sol	3 months aged sol	8 months aged sol
0.0	3.40	3.40	3.39
0.5	3.41	3.50	3.45
1.0	3.43	3.55	3.56
1.5	3.48	3.60	3.62
2.0	3.52	3.65	3.68
2.5	3.58	3.70	3.75
3.0	3.62	3.80	3.82
3.5	3.70	3.90	3.92
4.0	3.80	4.00	4.03
4.5	3.90	4.10	4.13
5.0	4.00	4.40	4.32
5.5	4.20	4.55	4.60
6.0	4.40	4.70	4.70
6.5	4.60	5.00	4.80
7.0	4.90	5.20	4.90
7.5	5.10	5.30	5.10
8.0	5.15	5.40	5.30
8.5	5.20	5.45	5.35
9.0	5.25	5.50	5.40
9.5	5.28	5.52	5.45
10.0	5.31	5.55	5.49

TABLE II

*pH Measurements for Sol A₁ (Purity 48·9) 10 ml. sol taken each time
(total volume 20 ml.)*

K ₂ SO ₄ in ml.	pH with N/300 K ₂ SO ₄		
	Fresh sol	3 months aged sol	8 months aged sol
0·0	4·30	4·30	4·10
0·5	4·36	4·50	4·20
1·0	4·44	5·10	4·30
1·5	4·50	5·90	4·40
2·0	4·60	6·10	4·50
2·5	4·80	6·30	4·70
3·0	5·00	6·50	5·10
3·5	5·20	6·60	5·25
4·0	5·50	6·70	5·40
4·5	5·80	6·80	5·60
5·0	6·00	6·90	5·90
5·5	6·10	7·10	6·00
6·0	6·15	7·20	6·02
6·5	6·20	7·22	6·04
7·0	6·25	7·24	6·06
7·5	6·30	7·28	6·08
8·0	6·35	7·31	6·10
8·5	6·39	7·35	6·10
9·0	6·41	7·40	6·10
9·5	6·43	7·40	6·10
10·0	6·45	7·40	6·10

In the following set of experiments the electrical conductivity of the systems with Sol B and Sol B₁ were also determined, in addition to the pH values. The last 3 columns show the value of K₁-K₂ where K₁ = specific conductivity of the mixture of sol and K₂SO₄ and K₂ is the specific conductivity of K₂SO₄ present in the mixture.

TABLE III

Volume of Sol B taken each time = 10 ml. (total volume 20 ml.)

K ₂ SO ₄ N/50 in ml.	pH			(K ₁ -K ₂ mhos.)		
	Fresh	2 months aged	8 months aged	Fresh	2 months aged	8 months aged
0	2.30	2.30	2.00	.03710	.04026	.04419
1	2.31	2.32	2.01	.03711	.03959	.04196
2	2.33	2.34	2.03	.03642	.03816	.04019
3	2.35	2.37	2.06	.03615	.03679	.03878
4	2.37	2.40	2.08	.03500	.03576	.03682
5	2.40	2.42	2.09	.03309	.03368	.03522
6	2.42	2.44	2.10	.03085	.03286	.03325
7	2.44	2.46	2.10	.02965	.03059	.03203
8	2.46	2.47	2.10	.02834	.02895	.03113
9	2.48	2.48	2.10	.02703	.02756	.02963
10	2.49	2.49	2.10	.02521	.02549	.02721

TABLE IV

Volume of Sol B₁ taken each time = 10 ml. (total volume 20 ml.)

K ₂ SO ₄ N/75 in ml.	pH			(K ₁ -K ₂ mhos.)		
	Fresh	2 months aged	8 months aged	Fresh	2 months aged	8 months aged
0	3.9	3.8	3.10	.002475	.003235	.005220
1	4.0	4.0	3.15	.001974	.002810	.004435
2	4.1	4.2	3.20	.001658	.002438	.003836
3	4.2	4.3	3.30	.001462	.002118	.003189
4	4.3	4.5	3.40	.001387	.001955	.003001
5	4.4	4.7	3.50	.001025	.001565	.002678
6	4.6	4.9	3.60	.000810	.001145	.001832
7	4.8	5.3	3.70	.000720	.000839	.001615
8	5.1	5.9	3.80	.000568	.000685	.001070
9	5.5	6.1	3.80	.000408	.000530	.000422
10	5.9	6.1	3.80	.000284	.000295	.000122

It was also thought necessary to investigate the changes in pH of a mixture of hydrous ferric oxide sample with hydrochloric acid, when varying quantities of K_2SO_4 is added to it. These results are shown in Table V.

TABLE V

Each time 10 ml. of the suspension of hydrous oxide was taken and was acidified with 10 ml. of hydrochloric acid of different strengths. Total volume made 45 ml. by the addition of potassium sulphate and water and pH measured.

K_2SO_4 added	0 ml.	5 ml.	10 ml.	15 ml.	20 ml.	25 ml.
Fresh precipitate						
(Fe_2O_3 + water) pH	.. 8.0	8.2	8.3	8.3	8.3	8.3
(Fe_2O_3 + N/10 HCl) pH	.. 2.1	2.2	2.4	2.5	2.6	2.7
(Fe_2O_3 + N/20 HCl) pH	.. 2.6	3.1	3.4	3.5	3.6	3.6
(Fe_2O_3 + N/40 HCl) pH	.. 3.7	6.4	6.6	6.65	6.7	6.7
(Fe_2O_3 + N/100 HCl) pH	.. 4.8	6.5	6.6	6.65	6.7	6.7
Two months aged precipitate						
(Fe_2O_3 + water) pH	.. 8.0	8.4	8.6	8.6	8.6	8.6
(Fe_2O_3 + N/10 HCl) pH	.. 1.9	2.2	2.4	2.6	2.7	2.7
(Fe_2O_3 + N/20 HCl) pH	.. 2.4	3.2	3.4	3.5	3.6	3.6
(Fe_2O_3 + N/40 HCl) pH	.. 3.4	5.6	5.9	6.1	6.2	6.2
(Fe_2O_3 + N/100 HCl) pH	.. 4.6	7.0	7.1	7.2	7.2	7.2
Six months aged precipitate						
(Fe_2O_3 + water) pH	.. 8.5	8.6	8.6	8.6	8.6	8.6
(Fe_2O_3 + N/10 HCl) pH	.. 1.8	2.0	2.2	2.4	2.5	2.5
(Fe_2O_3 + N/20 HCl) pH	.. 2.7	2.9	3.0	3.0	3.2	3.2
(Fe_2O_3 + N/40 HCl) pH	.. 3.9	5.5	5.8	5.9	6.0	6.0
(Fe_2O_3 + N/100 HCl) pH	.. 4.9	6.6	7.0	7.3	7.4	7.4

DISCUSSION

The mechanism of coagulation for a colloidal particle has been discussed by several authors.³ It is assumed that the hydrous ferric oxide is charged due to the preferential adsorption of hydrogen ions on the ferric ions on the colloidal surface, and the counterpart of the adsorbed chloride ions form the diffused double layer. Thus in the coagulation of the sol with electrolytes the precipitating ions enter into exchange adsorption with the counter ions in the outer diffused portion of the double layer in the particles. Thus a stage is reached when the oppositely charged ions actually reach the surface of the charged colloidal particles, resulting in the neutralization of the charge and when the extent of neutralization is sufficient, this leads to coagulation. Weiser and co-workers⁴ have shown that by the addition of potassium sulphate to a sol of ferric oxide more chloride ions become osmotically active in the sol. Therefore, the electrical conductivity of the sol must increase as more ions of the double layer become available for conduction. But our results show that the electrical conductivity goes on decreasing. The rise in the electrical conductivity at the beginning has been attributed to the release of hydrochloric acid on ageing, which has been confirmed by the decrease in pH value.

The following picture of the mechanism of coagulation by an electrolyte has been suggested in a previous paper.¹ When an electrolyte as potassium sulphate is added to the sol, the density of the diffused double layer of the oppositely charged ions, namely the anions, is increased, so that it is attracted by the positively charged surface of the colloidal unit and finally its electrical charge is discharged. As a result of this the hydrogen ions, which are the stabilizing ions now get absorbed on the surface, causing an increase of the hydroxyl ion concentration of the solution.

As the sol ages, there will be some rearrangement of the atoms. This has been confirmed by Weiser and co-workers,⁵ who had observed that freshly precipitated ferric oxide gel is amorphous to X-rays, but develops a hæmatite (Fe_2O_3) structure as the gel ages. Majorna⁶ observed magnetic and electric double refraction in an aged ferric oxide sol, which he has attributed to the larger size of the particles on ageing. Therefore on ageing the ferric oxide loses its adsorptive capacity and chemical reactivity, so that the generation of alkali by the process of charge neutralization cited above is less. It is thus expected that less of hydrogen-ions are to be adsorbed by aged sol, and less is the production of alkali. But the experimental results show that in a two or three months aged sol more of hydroxyl ions are produced. We are, therefore, led to believe that hydrous ferric oxide is also capable of

adsorbing some hydroxyl-ions,⁷ due to its amphoteric nature and that adsorbed hydroxyl-ions are released more easily by sulphate ions on the ageing of this hydrous oxide (*vide* Table V). On extreme ageing, *e.g.*, for eight months, the colloidal micelle loses the adsorptive capacity appreciably for hydrogen ions as well; so that the alkali generated in the process of coagulation visualised here is now less. The results, therefore, presented here fully support the contention that as the charge on the colloidal particles are gradually discharged by the oppositely charged ions, the colloidal units have a tendency to regain the same by the adsorption of such ions as may be present in the system capable of producing electric charge on it. This process continues till the surface of the colloid is completely saturated with the adsorbed ions imparting electric charge to the colloidal unit, which is neutralized to the critical value by the oppositely charged ions. It is for this reason that where colloidal solutions are prepared containing larger amounts of peptizing electrolyte as hydrochloric acid in ferric oxide colloid, the generation of alkalinity by the addition of sulphate is prominent.

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